

CLOSED-LOOP STRIPPING ANALYSIS METHOD

Closed-loop stripping analysis (CLSA) has been successfully applied in the past for the determination of volatile organic compounds (VOCs) of intermediate molecular weight, including many taste-and-odor species. Typically, the compounds are stripped from 1 L of water by a recirculating stream of air, and trapped on a carbon filter cartridge. Extraction of the cartridge to a small, 20 μ L volume produces unusually high concentration factors of 50,000:1 – enough to quantitate low ng/L levels. Although originally scheduled for the U.S. Environmental Protection Agency (USEPA) disinfection by-product (DBP) study, this technique proved less than desirable for continued research given the emerging successes of both solid phase extraction (SPE) and solid phase microextraction (SPME) techniques. It was discontinued during the Summer of 1999.

EXPERIMENTAL

Instrumentation

The instrument used for this work was a VG TS-250 medium resolution mass spectrometer (VG Tritech, Manchester, England) equipped with a Digital PDP-11/53 computer (Digital Equipment Corporation, Maynard, MA). Samples were injected using a CTC A200S autosampler (Leap Technologies, Chapel Hill, NC). A HP 5890 (Hewlett-Packard, Palo Alto, CA) gas chromatograph was used for separations and partially controlled by an Optic 2 injector (AI Cambridge, Cambridge, England).

Chromatography

A DB-1 column was used (30-m, 0.25-mm ID, 1- μ m film thickness) (J&W Scientific/Agilent, Folsom, CA). The GC oven temperature program used was based on EPA Method 551.1 (an initial temperature of 35 $^{\circ}$ C, which was held for 22 min, followed by an increase at a rate of 10 $^{\circ}$ C/min to 145 $^{\circ}$ C, which was held for 2 min; followed by an increase at a rate of 20 $^{\circ}$ C/min to 225 $^{\circ}$ C, which was held for 15 min).

General Procedure

The procedure for CLSA was taken from Standard Methods for the Examination of Water and Wastewater (20th ed., 1998). For standards, 900 mL of organic pure water (OPW) was placed into a 1-L glass stripping bottle. Seventy-two grams of sodium sulfate were added with rapid mixing until the salt was mostly dissolved. The sample was then spiked with a cocktail mix, covered, placed into a water bath at room temperature (22 $^{\circ}$ C), and stripped for 2 hours. The 1.5 mg carbon filter was extracted with dichloromethane, carbon disulfide (CS₂), or methyl *tertiary* butyl ether (MtBE) and brought to a final volume of 20 μ L, if needed. The infinitesimally small sample was transferred into a special conical-shaped autosampler vial for storage. After a 2 μ L injection to the GC, the remaining extract was covered with a fresh Teflon cap and stored in the freezer for future reference. A detailed description of the method can be also found at Krasner *et al.* (1983).

RESULTS AND DISCUSSION

Initial DBP Testing - Extraction Efficiency

Stripping efficiencies can be optimized by adjusting stripping time, temperature, and use of salt to increase the ionic strength of the water. A preliminary check of DBP compatibility was done using a mixture of DBPs spiked in organic pure water. The spiking mix (5 μ L of the 200 ppm mixture) was added to 900 mL of pure water to give an actual concentration of 1.1 μ g/L in the water. At 100% analyte recovery, this is equivalent to a 50-ppm unextracted standard. Stripping time was two hours.

Table 1. Extraction efficiency of select DBPs

Compound	RT (min)	No Salt CS ₂	No Salt CS ₂ DUP	72 g Salt CS ₂	72 g Salt CS ₂ DUP	72 g Salt MeCl ₂	72 g Salt MeCl ₂ DUP
chloroacetonitrile	7.3	ND	ND	ND	ND	ND	ND
chloropropanone	7.9	ND	ND	ND	ND	ND	ND
carbon tetrachloride	8.7	6%	ND	ND	9%	3%	15%
bromoacetonitrile	15.2	ND	ND	ND	ND	ND	ND
dichloriodomethane	24.8	14%	15%	24%	19%	25%	44%
1,3-dichloropropanone	27.5	ND	ND	ND	ND	ND	ND
bromochloriodomethane	29.6	37%	23%	50%	36%	44%	71%
1,1,3-trichloropropanone	31.0	ND	ND	ND	ND	ND	ND
chlorodiodomethane	33.2	37%	22%	49%	40%	57%	76%
bromodiodomethane	35.7	26%	19%	60%	40%	47%	61%
hexachloropropanone	37.4	ND	ND	ND	ND	ND	ND
iodoform	38.1	8%	6%	22%	14%	21%	24%

This preliminary check of the CLSA method pointed out potential problems that would need to be addressed. First, the results were highly irreproducible for duplicate analyses without any internal standard. The sample concentrations listed in Table 1 were obtained from raw area counts of the compound peaks. There can be many variables introduced during the stripping procedure to cause such a wide variance in results, such as minute air leaks in the stripping apparatus, differences in the filter flow rates (age of filter, contamination), temperature differences during stripping, and analyte loss during the final extraction. For some haloketones and haloacetonitriles (chloropropanone, 1,3-dichloropropanone, 1,1,3-trichloropropanone, chloroacetonitrile, and bromoacetonitrile), there were no detectable recoveries. For the iodinated THMs and carbon tetrachloride, results showed that the use of salt improved the stripping efficiency. Also, dichloromethane was a better solvent compared to carbon disulfide.

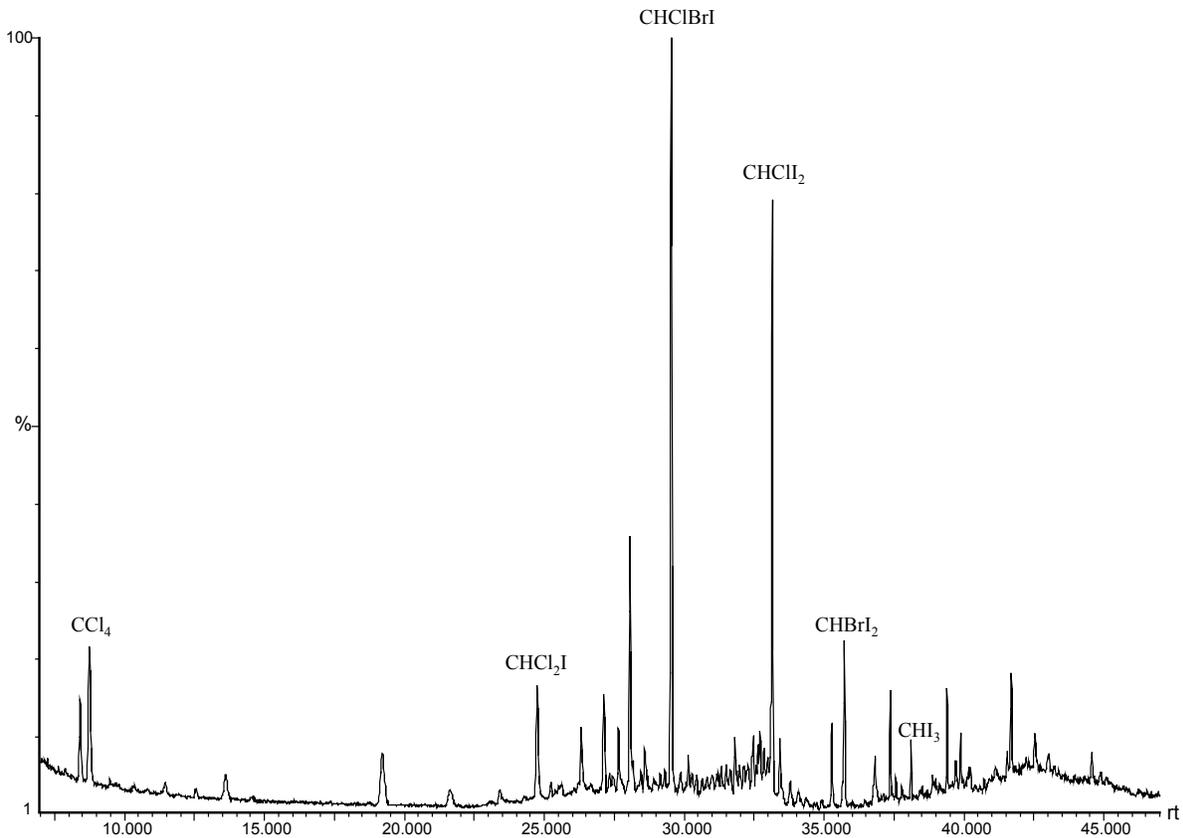


Figure 1. Two-hour closed-loop stripping analysis of iodinated THMs and carbon tetrachloride. Elution solvent was dichloromethane.

Figure 1 shows the best case scenario for iodo-THMs and carbon tetrachloride, utilizing 72 grams of sodium sulfate and dichloromethane for extraction. Stripping time was 2 hours.

Traditional DBPs

Initial attempts to apply closed-loop stripping analysis to the new DBPs that are part of this project failed to yield immediate results for any compounds other than iodinated species and carbon tetrachloride. The targeted compounds included chloropropanone, 1,3-dichloropropanone, 1,1,3-trichloropropanone, hexachloropropanone (later found to immediately hydrolyze in water), bromoacetonitrile, and chloroacetonitrile.

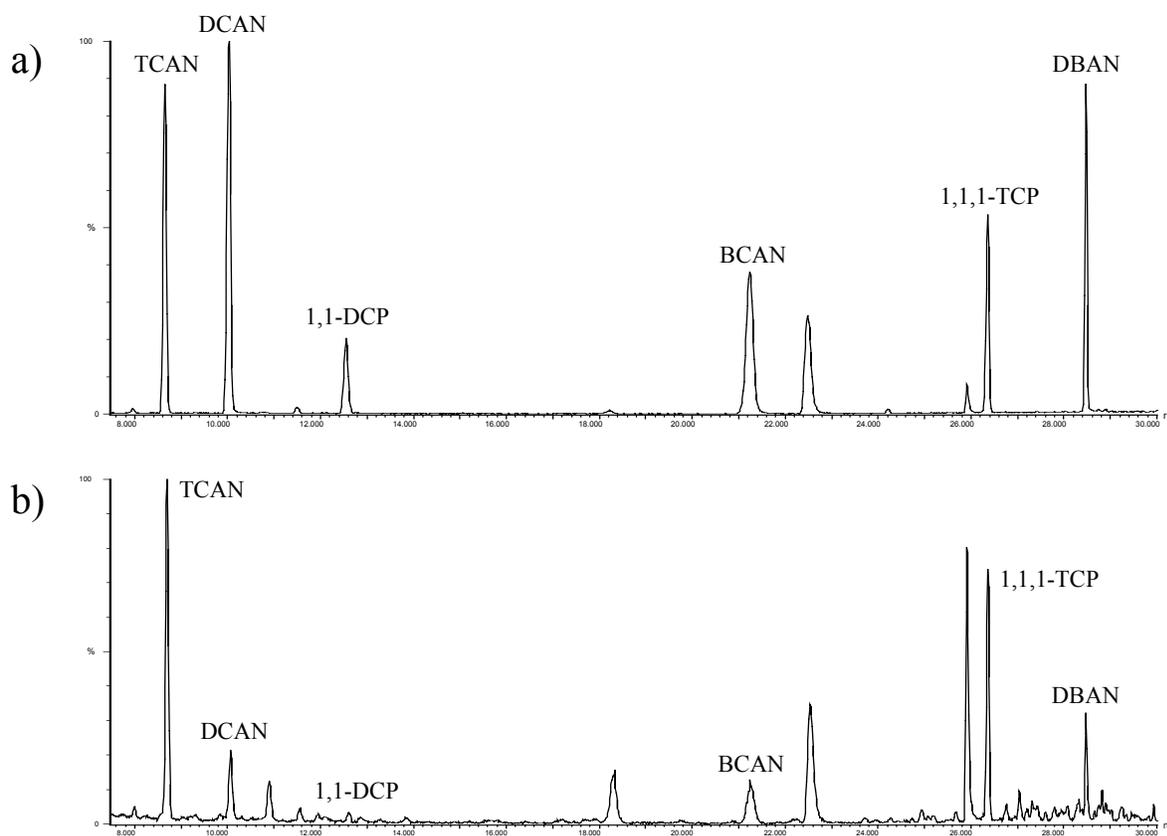


Figure 2. a) Direct injection of 200 ppm of DBP mixture for comparison. b) CLSA extract of DBP mixture in MtBE.

It was suggested that some of the EPA method 551.1 DBPs should be attempted since there was some evidence that it should be possible to strip these compounds (Croue and Reckhow 1989). Therefore, the following standards were obtained and analysed by CLSA: dichloro-, dibromo-, and trichloroacetonitrile, and 1,1-dichloro-, and 1,1,1-trichloropropanone. Results from these compounds were more promising. A series of experiments was performed to evaluate the effect of extraction solvent and stripping time for the compounds. All of the compounds were spiked both with the DBP mixture and an added 1-chlorooctane internal standard/surrogate. For consistency and ease of results interpretation, all samples were stripped on the same apparatus and on the same day. Three solvents were tested, including MtBE, dichloromethane, and carbon disulfide. A 30-min stripping time was also evaluated as an alternative to the traditional 1-2 hour time.

The MtBE solvent peak eluted at 4 min and continued until about 5.5 min, with tailing. Quantitative peaks occurred after 7 min and continued throughout the 50-min run. The 1-chlorooctane internal standard eluted at 34 min and was not shown in Figure 2. All peaks were identified using their NIST library mass spectra.

Overall, MtBE was best at removing the compounds from the carbon filter, followed by MeCl_2 , and then CS_2 . An additional benefit of using MtBE is that it allows extracts to be run on a GC equipped with an electron capture detector (ECD), which is not possible for chlorinated solvents. In addition, it was confirmed that a 1-hour strip was preferred over a 30-min strip time,

although there is a point of diminishing returns. Generally, anything over two hours does not increase analyte recoveries significantly.

The use of higher stripping temperatures improved stripping efficiency. However, attempts at 40 °C were unsuccessful because of moisture condensation onto the carbon filter. Despite attempts to heat the entire air system using heater tape to avoid cold spots, the large volume of humid air moving through the system inevitably spoiled any attempts to produce successful results. Commercially-designed systems (e.g. Mass Evolution, Inc., Houston, TX) can use slightly wider glass cartridge holders and heating blocks to allow higher temperature operation.

CONCLUSIONS

At the start of this work, many of the DBPs that were planned for the Nationwide DBP Occurrence Study had yet to be received. This work represents only a portion of the compounds that could have been tested. But, based on these preliminary results, it seems unlikely that CLSA would have been a good universal screening device for new DBPs (i.e. limited compatibility, large sampling requirement, poor reproducibility). Table 2 lists the compounds tested and whether they were amenable to closed-loop stripping analysis.

REFERENCES

- Croué, J.-P., and D. A. Reckhow. Destruction of chlorination byproducts with sulfite. *Environmental Science & Technology* 23(11):1412 (1989).
- Krasner, S. W., C. J. Hwang, and M. J. McGuire. *Water Science & Technology* 15: 127 (1983).
- Munch, D. J., and D. P. Hautman. Method 551.1. Determination of Chlorination/Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron Capture Detection. *Methods for the Determination of Organic Compounds in Drinking Water, Supplement III*, EPA-600/R-95/131. Cincinnati, OH: U.S. Environmental Protection Agency, 1995.
- Standard Methods for the Examination of Water and Wastewater, 20th ed.*; American Public Health Association: Washington, D.C., 1998.

Table 2. Summary of compounds tested for closed-loop stripping analysis

Compound	CLSA Extraction?
Iodomethanes	
Dichloriodomethane	YES
Bromochloriodomethane	YES
Dibromiodomethane	YES
Chlorodiiodomethane	YES
Bromodiiodomethane	YES
Triiodomethane (iodoform)	YES
Haloacetonitriles	
Chloroacetonitrile	NO
Bromoacetonitrile	NO
Dichloroacetonitrile	YES
Bromochloroacetonitrile	YES
Dibromoacetonitrile	YES
Trichloroacetonitrile	YES
Haloketones	
Chloropropanone	NO
1,1-Dichloropropanone	NO
1,3-Dichloropropanone	NO
1,1,1-Trichloropropanone	YES
1,1,3-Trichloropropanone	NO
Misc. Compounds	
Carbon tetrachloride	YES